



Photodegradation of chloroacetic acids over bare and silver-deposited TiO₂: Identification of species attacking model compounds, a mechanistic approach

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ABSTRACT

Photocatalytic degradation of chloroacetic acids (CIAAs) over various bare and silver-deposited Degussa P25 TiO₂ particles was studied. Adsorption measurements carried out using TiO₂ photocatalysts of different origin demonstrated significant dependence of the adsorption efficiency on the nature of semiconductor particles and on the number of chlorine atoms of the substrate. Irradiation of the reaction mixtures containing monochloroacetic acid (MCA), dichloroacetic acid (DCA) and trichloroacetic acid (TCA), respectively, over P25 titania were performed under anaerobic and aerobic conditions. The progress of photocatalysis was followed by measuring the substrate concentration, the total organic carbon content (TOC) and the concentration of the chloride ion in the liquid phase of reaction mixtures. Opposite trends in the photodecomposition rate of the substrates were obtained for aerobic $\nu_{\text{MCA}} \approx \nu_{\text{DCA}} > \nu_{\text{TCA}}$ and for anaerobic experiments $\nu_{\text{TCA}} > \nu_{\text{DCA}} > \nu_{\text{MCA}}$, respectively. The evolved CO₂ was also measured under aerobic photodecomposition of DCA. Important role of hydroxyl radicals in the photomineralization of mono- and dichloroacetic acid was confirmed by using coumarin (COU) as a hydroxyl radical scavenger and oxalic acid as an efficient scavenger for holes. Silver deposition onto the TiO₂ surface enhanced the efficiency of the semiconductor by a factor of 4 for the photooxidation of TCA and by a factor of 1.4 for DCA and MCA.

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1. Introduction

Application of TiO₂ photocatalysis has been widely reported as a promising alternative technology for removal of various organic and inorganic pollutants from contaminated water and air [1–7]. Chloroacetic acids are important medical intermediates and organic materials [8]. These compounds are widespread in the environment, and often occur in industrial waste as pollutants and in chlorinated drinking waters as major chlorination by-products as well [9–13]. CIAAs are carcinogenic and mutagenic [10]. Moreover, they cannot be completely decomposed by biotechnologies [12,13]. In this respect investigation of the applicability of the heterogeneous photocatalysis for degradation of CIAAs and the study of the mechanism of these photoreactions are considered as a research of great importance.

Decomposition of mono-, di- and trichloroacetic acid in aqueous titania suspensions was extensively studied by several research groups [13–19]. Different experimental evidences, hence various proposals have been reported concerning the reaction mechanism, particularly on the primary steps of the photocatalytic decomposition of CIAAs. It has been concluded that two types of

reactions may be responsible for the TiO₂-mediated photodegradation of chloroacetic acids: (1) direct reactions between the photogenerated charge carriers and the organic molecules [16,20–22] and (2) reactions of hydroxyl radicals or other oxygen containing radicals with the organic molecules [15,23,24]. MCA and DCA are readily decomposed over UV-irradiated TiO₂ catalyst in aqueous media to CO₂ and HCl [14,15]. On the other hand using bare TiO₂ TCA is degraded with a very low efficiency [15]. TCA has no C–H bond, and such a molecule has been found to be hardly reactive in TiO₂-based photocatalytic systems [15,24].

Various approaches have been attempted to enhance the photocatalytic efficiency and visible light utilization of TiO₂ [7]. Doping and partially coating the catalyst's surface with noble and transition metals (such as Cu, Fe, Ag, Cr, Pt, Pd, Rh, Ir, Os and Au) have been proved to be promising [17,25–28]. Photocatalytic deposition of nanosized silver clusters offered some advantages, such as a simple procedure and relatively low cost [26]. The silver clusters at the semiconductor surface can act as electron traps during the illumination [29–31]. Due to the electronic contact between the deposited metal and the semiconductor (SC) the electrons are removed from TiO₂ into the vicinity of metal clusters resulting in the formation of Schottky-barriers at each Ag–TiO₂ contact regions. This facilitates the charge separation and hence inhibits the recombination of photogenerated electron–hole pairs [26,32–34]. Substantial amount of work have reported the effect of

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silver deposition on the photodegradation rate of organic substrates [26,31,35–46]. In a recent study Tran et al. [44] claim to predict the effect of silver deposition on TiO_2 by considering the molecular structure of the substrate, and they also suggest that an enhanced photocatalytic activity can be observed for those compounds that predominantly oxidized by holes instead of hydroxyl radicals [44,47]. In this respect silver-deposited TiO_2 can be applied not only to increase the photooxidation rate of the organics but also to provide data for revealing the mechanism of the studied photoreaction. In principle, some valuable additional information on the mechanism of photocatalytic degradation of CIAAs can be obtained using scavengers for hole (e.g. oxalic acid) and for hydroxyl radical (e.g. COU), respectively in competitive kinetic experiments.

The aim of the present contribution is to deepen our knowledge on the photodecomposition mechanism of CIAAs occurring over TiO_2 nanoparticles exposed to photons of higher energy than the band gap of the semiconductor. Attention has been focused to reveal the primary electron transfer reaction and the role of the hydroxyl radical formed by one of these steps. We propose a strategy based on: (i) the comparison of the rate of photoreactions occurring under anaerobic and aerobic conditions; (ii) the analysis of the results of competitive kinetic measurements using COU as a component, which is weakly adsorbed on TiO_2 surface and acts as hydroxyl radical scavenger producing highly fluorescent 7HC and (iii) the application of silver-deposited TiO_2 for increasing the rate of photoreaction of the reactant that can be directly attacked by e^-_{CB} or h^+_{VB} generated by photon absorption. The different affinity of MCA, DCA and TCA to the TiO_2 surface is also exploited for confirming the proposed mechanism.

2. Experimental

2.1. Materials

The titanium dioxide samples used in experiments were obtained from Degussa (P25: 70% anatase, 30% rutile; with a surface area of $50 \text{ m}^2 \text{ g}^{-1}$), from Aldrich (mainly anatase, with a surface area of $9.6 \text{ m}^2 \text{ g}^{-1}$) and from Fluka (mainly rutile, with a surface area of $9.7 \text{ m}^2 \text{ g}^{-1}$).

Monochloroacetic acid, dichloroacetic acid and trichloroacetic acid of the purest grade were purchased from Fluka. Coumarin (COU) and 7-hydroxycoumarin (7HC) of the purest grade obtained from Sigma–Aldrich and Carlo Erba, respectively, and were used without further purification. All other reagents such as Ag_2SO_4 , AgNO_3 , $(\text{NH}_4)_2\text{SO}_4$, KMnO_4 , NaClO_4 , KCl , $\text{Ba}(\text{OH})_2$ were purchased from Reanal (Hungary) and were used without further purification. Each chemical was dissolved in high purity water and used for the experiments. The high purity water was double distilled and then purified with a Milli-Q system.

2.2. Adsorption measurements

Adsorption studies of CIAAs were performed in suspensions in dark using various titania catalysts (pure rutile, pure anatase, and Degussa P25). The initial concentration of chloroacetic acids was 1 mM, which was checked by HPLC method using analytical measuring curves (see [Supplementary materials, FigS2](#)). 500 cm^3 of the solutions were transferred into a 750 cm^3 flask, then 500 mg TiO_2 was added to solutions. The suspensions were continuously stirred in dark and during this procedure 5 cm^3 samples were taken from time to time. The samples were filtered as given vide infra (Section 2.3) then the concentration of CIAAs in the homogeneous solutions was measured by HPLC. The concentration of chloroacetic acids in aqueous phase decreased continuously, then after 40 min stirring it was found to be constant.

2.3. Photoreactor and photocatalytic experiments

Photochemical experiments were performed in a medium scale ($V = 2.5 \text{ dm}^3$) photochemical reactor. The reactor was developed for irradiation of heterogeneous reaction mixtures circulated by continuously fed air or other gases, such as Ar as described earlier [38]. The flow rate of gases was $40 \text{ dm}^3 \text{ h}^{-1}$. The photon flux of the internal light source (40 W , $\lambda_{\text{max}} = 350 \text{ nm}$) was determined by potassium tris(oxalato)ferrate(III) chemical actinometry [48] and it was found to be $(6.95 \pm 0.04) \times 10^{-6} \text{ mol photon s}^{-1} \text{ dm}^{-3}$. The initial volume of the reaction mixture was set to be 2.5 dm^3 prior to irradiation in all experiments. The initial concentration of TiO_2 (rutile, anatase, P25) was 1 g dm^{-3} in the photochemical experiments. The initial concentration of MCA, DCA, and TCA was adjusted to be 1 mM. The concentration of coumarin was set to 10^{-4} M as optimal value for the experiments. 0.1 M constant ionic strength was adjusted by NaClO_4 .

Silver-deposited TiO_2 was prepared by photocatalytic reduction of AgNO_3 or Ag_2SO_4 ($[\text{Ag}^+] = 10^{-4} \text{ M}$) prior to use it as photocatalyst for the degradation of the organics. The suspension containing 1 g dm^{-3} TiO_2 was irradiated in the photoreactor used for photodegradation of chloroacetic acids. The color of the suspension was observed to be changed from white to pale-brown indicating the reduction and deposition of the Ag on TiO_2 . The photodeposition was completed within 40 min, which was checked by the procedure described in details elsewhere [38]. The irradiated mixture was centrifuged and then washed by high purity water given in Section 2.1. These procedures were repeated at least three times to obtain nitrate or sulfate free washing water. Then Ag– TiO_2 photocatalyst was dried at 120°C .

2.4. Analytical procedures

Before and during the continuous illumination 5 cm^3 samples were taken from the reaction mixture through a septum with a syringe. Samples containing TiO_2 were filtered through a Millipore Millex-LCR PTFE $0.45 \mu\text{m}$ membrane filter. The concentration of the formed chloride anions was measured by potentiometric method applying Radelkis OP-271/1 chloride ion selective electrode and Ag/AgCl reference electrode. Analytical measuring curve is given in [Supported materials \(FigS1\)](#). The concentration of chloroacetic acids was determined by high performance liquid chromatography (HPLC) using analytical calibration curves (see [FigS2](#)). The HPLC system was a Liquochrom with ChromSphere BST SI 100-S 10 C18 column. The eluent was 0.15 M $(\text{NH}_4)_2\text{SO}_4$ aqueous solution. Flow rate of the eluent was 0.7 ml min^{-1} for all analysis. The UV detection was carried out at $\lambda = 210 \text{ nm}$. The photomineralization of chloroacetic acids was also followed by measuring the total carbon (TC) content and the total inorganic carbon content (IC) of the irradiated samples by means of a TOC-TN1200 analyzer (Thermo electron Corporation). Six parallel samples of $100 \mu\text{l}$ volume were taken by a micro-syringe from the aqueous phase of the reaction mixture withdrawn from the reactor at specific irradiation time and these samples were measured into the analyzer. Total organic carbon (TOC) content was determined from the average of the six TC and IC values. The changes in pH values of the samples were followed by using WTW pH 9 type apparatus with Sen Tix 41 electrode. The fluorescence emission spectrum (excited at 332 nm) of 7-hydroxycoumarin was measured by a PerkinElmer LS 50B luminescence spectrometer. Both the emission and excitation slits were set to 5.0 nm during the measurements and the temperature of the solution was adjusted to 20.0°C . Absorption spectra of coumarin, 7-hydroxycoumarin and the liquid phase of the reaction mixture was recorded by an Analytik Jena Model SPECORD S 100 spectrophotometer. The concentrations

of 7-hydroxycoumarin formed and that of the coumarin disappeared were determined by using analytical calibration curves (see FigS3–4). The concentration of oxalic acid in the liquid phase of the reaction mixture was determined by classical permanganometry.

3. Results and discussion

3.1. Adsorption studies

In principle, adsorption and desorption of reactants and intermediates have great influence on the efficiency of the overall degradation process in TiO_2 -mediated photocatalytic procedures. Organic compounds chemisorbed on TiO_2 surface directly react with photogenerated holes, while reactants weakly or non-adsorbed in aqueous environment are generally attacked by radicals such as $\cdot\text{OH}$, or $\text{O}_2^{\cdot-}$ at the surface or in the bulk of aqueous phase. Thus adsorption experiments are considered as essential for a detailed study in this field. Fig. 1 demonstrates the equilibrium concentration of CIAAs adsorbed on the surface of various TiO_2 catalysts at slightly acidic conditions ($\text{pH} \sim 3$).

Although the equilibrium concentration of adsorbed CIAA strongly depends on the nature of the TiO_2 and the number of chlorine atoms of CIAA, the tendencies are clear. Namely, the equilibrium concentration significantly decreases with the number of chlorine atom for all investigated TiO_2 and it is also decreasing according to $\text{P25} > \text{A} > \text{R}$. It should be noted that the equilibrium concentration of TCA adsorbed is lower than $10 \mu\text{M}$ for all catalysts.

It is generally accepted that interaction between carboxylic acids and TiO_2 surface occurs via carboxylate group and the strength of this interaction depends on the pH. For example, FTIR studies have revealed [17] that in acidic solution at $\text{pH} < 4$, bi-dentate complexes of DCA (both oxygen atoms of the DCA carboxylic group are coordinated to the surface) predominate in the system. The surface of TiO_2 contains amphoteric titanol groups, the value of the pH of zero point of charge (pH_{zpc}) for Degussa P25 is equal to 6.25 [1]. If the pH of media is above 6.25, the surface is negatively charged while at lower pH than 6.25 the surface of semiconductor is positively charged. The species in reaction mixture generally prefer the adsorption to the opposite charged surface.

The dominant form of CIAAs in the aqueous phase of $\text{pH} \approx 3$ is the deprotonated species due to the relatively small pK_a values ($\text{pK}_{a(\text{MCA})} = 2.87$, $\text{pK}_{a(\text{DCA})} = 1.25$, and $\text{pK}_{a(\text{TCA})} = 0.70$). Since, the mole fraction of the anionic form in aqueous phase increases with the number of chlorine atom of CIAA at pH 3 and the adsorption ability shows an opposite trend, the dominance of electrostatic interaction between the positively charged TiO_2 surface and the negatively charged anionic CIAAs can be excluded for DCA and especially for TCA. On the other hand, it is reasonable to suppose a

significant contribution of the hydrogen bonding between the carboxyl group of MCA and the surface OH group of TiO_2 to the stability of surface complex. This interaction is weakening with the number of chlorine atom of CIAAs, which is in accordance with the pK_a values.

3.2. Photodegradation of CIAAs over bare TiO_2 under anaerobic conditions

The photodegradation of CIAAs was investigated under anaerobic condition using P25. These experiments clearly demonstrate an apparently zero order decomposition of substrates and a significant increase in the rate of photodecomposition with the number of chlorine substituent (Fig. 2). It is important to note that this trend is similar to that of the rate of electron scavenging reactions measured in aqueous solutions [49] and it is opposite to the rate of heterogeneous photodecomposition observed under aerobic conditions (see vide infra).

These findings can be explained by the rate determining nature of the electron transfer from the conduction band to the organic molecules. This primary reaction step is significantly slower than that of $\{\text{h}^+_{\text{vb}}; \text{e}^-_{\text{cb}}\}$ recombination. Consequently, the chloride ion is formed by low efficiency. The rate coefficient of electron scavenging reaction of CIAAs in homogeneous aqueous solution significantly increases with the number of chlorine atoms. Thus TCA is the most efficient electron acceptor among CIAAs. The primary electron transfer is followed by the formation of chloride ion and $\text{Cl}_{x-1}\text{C}^*\text{H}_{3-x}\text{COO}^-$ radical of high reactivity. On the other hand, the yield of the photogenerated holes avoided the charge carriers' recombination is also very low. These species are trapped at the surface of semiconductor particle resulting in trapped holes (h^+_{surf}) that cannot oxidize water to hydroxyl radical. Therefore the decomposition of MCA and DCA due to the hydrogen atom abstraction by hydroxyl radical can be excluded. The oxidation potential of trapped hole is 1.5 V [50] which is not enough to abstract hydrogen atom from DCA and MCA, hence h^+_{surf} cannot contribute to the degradation of these compounds. On the other hand, it can readily react with the radical (R1) formed by reaction (1). The radical R1 can be also disappeared by radical–radical reaction resulting in R1–R1. However, the efficiency of this reaction should be rather small due to the low concentration of R1 under the experimental conditions.



3.3. Photodegradation of CIAAs over bare TiO_2 under aerobic conditions

In correlation with the results of adsorption measurements Degussa P25 has been proved to be the most efficient photocatalyst

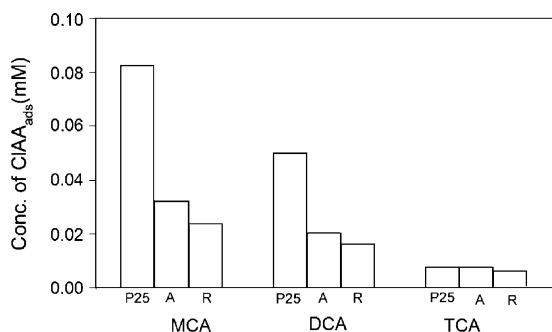


Fig. 1. Equilibrium concentration of CIAAs adsorbed on the surface of various TiO_2 at $[\text{CIAA}]_0 = 1 \text{ mM}$ and $C_{\text{TiO}_2} = 1 \text{ g dm}^{-3}$; Degussa P25 (P25), pure anatase (A) and pure rutile (R) TiO_2 .

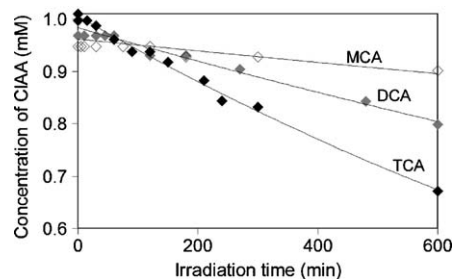


Fig. 2. Change in the concentration of MCA (\diamond), DCA (\blacklozenge) and TCA (\blacklozenge) under irradiation of the reaction mixture of $[\text{CIAA}]_0 = 1 \text{ mM}$ and $C_{\text{TiO}_2} = 1 \text{ g dm}^{-3}$ using argon.

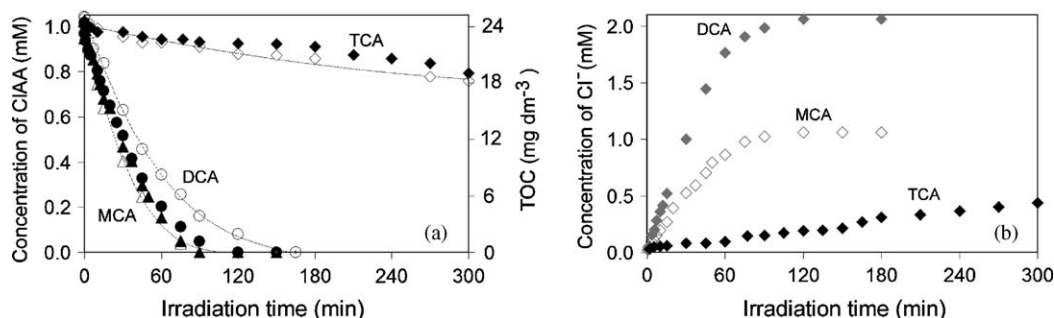


Fig. 3. Change in the concentration of CIAAs {MCA (▲), DCA (●), TCA (◆)} and TOC {MCA (△), DCA (○), TCA (◇)} (a) and that of in the chloride concentration {MCA (◇), DCA (○), TCA (◆)} (b) under irradiation of aqueous suspension of MCA, DCA and TCA, respectively, in the presence of P25 TiO₂. The initial concentration of CIAAs and TiO₂ was adjusted to be 1 mM and 1 g dm⁻³, respectively.

among the used bare TiO₂ semiconductors (rutile, anatase and P25) for oxidation of MCA, DCA and TCA (FigS5–S7) in aerobic conditions. The decomposition of MCA and DCA in aerated suspension is much faster than in Ar saturated suspension (compare Figs. 2 and 3). On the other hand, the rate of TCA's disappearance under air is similar to that of observed under Ar. This experimental fact is in accordance with the observations of Chemseddine and Boehm [15]. Moreover, the stoichiometric decrease of TOC in the liquid phase indicates that there is no significant amount of intermediate containing carbon atom(s) during the photodecomposition of TCA. It suggests that the rate determining primary electron transfer step is followed by fast reaction steps leading to the complete mineralization of the TCA. It is also confirmed by the time dependence of chloride formation, which can be regarded stoichiometric (nearly three chloride ion is formed under decomposition of one TCA). In conclusion, it is reasonable to assume that the first reaction step under aerobic as well as anaerobic photodegradation of TCA is the release of a chloride ion.

For aerobic conditions this can be explained by a special electron transfer property of molecular oxygen at the surface of the excited TiO₂ particle. According to this assumption O₂^{•-} radical formed by reaction (2) can subsequently transfer the electron to the TCA approaching the surface of TiO₂. This role of molecular oxygen has been proposed by Giménez et al. [51].



Under our experimental conditions MCA is totally degraded within 90 min irradiation and the complete disappearance of DCA requires a slightly longer irradiation period (ca. 120 min). In both cases all organic chlorine is converted into chloride ion, which is clearly demonstrated by Fig. 3. On the other hand TCA decomposes very slowly; after 5 h irradiation of TCA containing suspension only 20% of the organic substrate has been degraded. The initial rate of chloride production and that of the disappearance of the chloroacetic acid obtained by linear and polynomial fitting, respectively, are summarized in Table 1.

The photodecomposition rate of MCA in the presence of oxygen is more than 200 times higher than that of in anaerobic conditions.

So the mechanism of MCA decomposition in the two conditions should be significantly different. Under Ar, the reaction (1) competing with the charge recombination of high efficiency results in a few holes. Most of these holes are trapped and the trapped holes (h^+_{surf}) cannot oxidize water to form hydroxyl radicals. Hence the concentration of hydroxyl radicals that could efficiently attack the MCA molecules should be very low. On the other hand, under aerobic conditions the photon generated conduction band electrons are efficiently transferred to molecular oxygen adsorbed/approaching onto the surface of the semiconductor particle. Thus, a considerable amount of free holes remain. Some of them are trapped at the surface. The number of active sites for trapping the holes is determined by the crystalline structure of TiO₂ particle and its specific surface area, which depends on the size of the particle and the nature of the surface too. It is expected, that at high light intensity and using efficient electron acceptors of high concentration a saturation of trapped hole can be easily achieved. A further increase in the formation rate of the holes provides a significant increase in the fraction of 'not trapped holes'. The yield of the 'not trapped holes' is expected to be rather high in aerobic condition. Thus the hydroxyl radical formation by reaction (3) must be very efficient.



The hydroxyl radicals readily react with MCA to produce radical ClC[•]HCOO⁻ (reaction (4)):



The radical (ClC[•]HCOO⁻ = R2) can be disappeared by various radical–radical reactions such as R2 + R2, R2 + R1, R2 + O₂^{•-} and R2 + •OH. The rate of disappearance of MCA and that of chloride formation from MCA are the same within the experimental error and we could not detect carbon containing intermediates. This experimental fact can be explained by the negligible influence of R2 + R2 and R2 + R1 reaction, respectively. On the other hand, R2 + O₂^{•-} reaction should efficiently lead to the formation of chloride ion.

The decrease in TOC is significantly delayed to the disappearance of DCA (Fig. 3a). It clearly demonstrates the formation of

Table 1

Reaction rates measured under irradiation of reaction mixture containing MCA, DCA and TCA, respectively, and P25 (1 g dm⁻³).

	Initial rate ^a (M ⁻¹ min ⁻¹)			Comment
	MCA	DCA	TCA	
Disappearance of CIAA	9.2 × 10 ⁻⁸	2.8 × 10 ⁻⁷	5.5 × 10 ⁻⁷	Anaerobic condition
Disappearance of CIAA	2.0 × 10 ⁻⁵	1.8 × 10 ⁻⁵	5.8 × 10 ⁻⁷	Aerobic condition
Cl ⁻ formation	1.8 × 10 ⁻⁵	4.2 × 10 ⁻⁵	1.5 × 10 ⁻⁶	Aerobic condition

^a The estimated error of initial rate is about 8%.

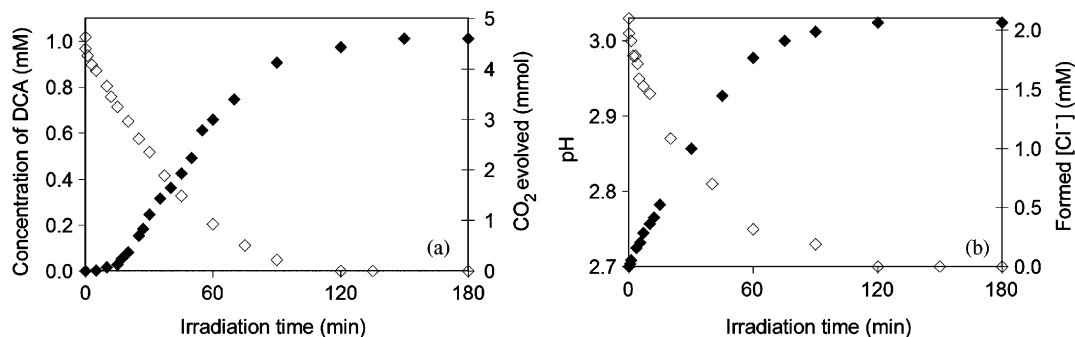


Fig. 4. Formation of CO₂ (◆) and the disappearance of DCA (◇) (a) and the change of pH (◇) and formation of Cl[−] (◆) (b) during the course of photodegradation of DCA over Degussa P25 TiO₂; [DCA]₀ = 1 mM, C_{TiO₂} = 1 g dm^{−3}.

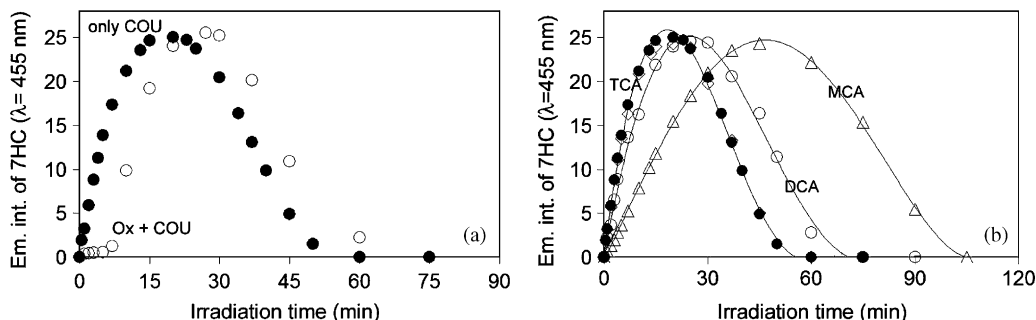
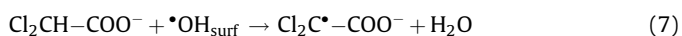
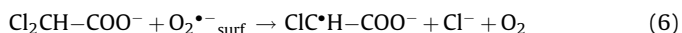


Fig. 5. Change of the emission intensity of 7HC measured at 455 nm (λ_{ex} = 332 nm) under irradiation of TiO₂ containing suspensions (C_{TiO₂} = 1 g dm^{−3}): (a) (○) [Oxalic acid]₀ = 0.1 mM and [COU]₀ = 0.1 mM, (●) [COU]₀ = 0.1 mM; and (b) (●) [COU]₀ = 0.1 mM, (○) [COU]₀ = 0.1 mM and [TCA]₀ = 1 mM, (△) [COU]₀ = 0.1 mM and [DCA]₀ = 1 mM, (▽) [COU]₀ = 0.1 mM and [MCA]₀ = 1 mM.

carbon containing intermediates under decomposition of DCA, which is confirmed by the induction period of the CO₂ evolution (Fig. 4a). Fig. 4b compares the pH change with the formation of chloride ions.

The increase in the disappearance rate of DCA due to the change in conditions from anaerobic to aerobic is considerable. However, it is significantly smaller than that of observed for MCA (~65 times compared to ~220). It is attributed to the contribution of the following reaction steps (reactions (5)–(7)) to the degradation of DCA.



It is reasonable to suppose that the role of reaction (7) in the decomposition of DCA is significantly higher than that of (5) and (6), and the rate of direct electron transfer is slower than that of occurring through molecular oxygen. It should be emphasized that the molecular oxygen mediated electron transfer to the DCA is expected to be slower than that of to the TCA. On the other hand the hydroxyl radical attack on DCA is not so effective than that of on MCA. It is demonstrated by the results of competitive kinetic measurements using COU as luminescent probe for detecting and measuring hydroxyl radicals [52–54]. Fig. 5 shows the luminescence intensities originating from the excited 7HC under irradiation of various reaction mixtures containing P25 TiO₂. We demonstrated recently [54] that 7HC is formed as an intermediate under heterogeneous photocatalysis of COU in aerobic conditions. Hydroxyl radicals have been proved to be responsible for the formation of photoluminescent 7HC, while molecular oxygen and/or the superoxide anion are the species that play crucial role in the disappearance of 7HC. Addition of oxalic acid as a typical hole scavenger [38,44,45] to the aqueous

suspension of COU and TiO₂ results in a significant delay in the formation of 7HC (Fig. 5a). Because of the very fast electron transfer from the oxalic acid adsorbed at the surface to the valence band hole, the reaction of hole with water molecules to produce hydroxyl radical is strongly suppressed. This inhibition of hydroxyl radical formation is finished at the complete oxidation of the oxalic acid. Such a delay has not been observed under photocatalytic degradation of COU in the presence of MCA, DCA or TCA (Fig. 5b) confirming that CIAAs do not react directly with photogenerated holes. On the other hand, a significant decrease in the rate of 7HC formation has been measured in the presence of MCA. DCA causes rather small changes in the rate of 7HC production, while such an effect could not be observed for TCA. These findings clearly confirm that the hydroxyl radical attack on MCA and DCA plays important role in the photodegradation of these species [55].

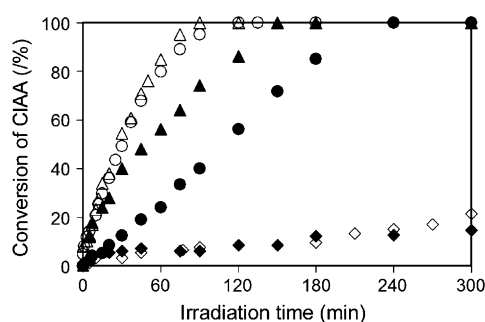


Fig. 6. Conversion of chloroacetic acids under irradiation of the suspensions containing MCA (△), DCA (○), and TCA (◇), respectively and that of the mixture of MCA (▲), DCA (●) and TCA (◆); [MCA]₀ = 1 mM, [DCA]₀ = 1 mM, [TCA]₀ = 1 mM, C_{TiO₂} = 1 g dm^{−3}.

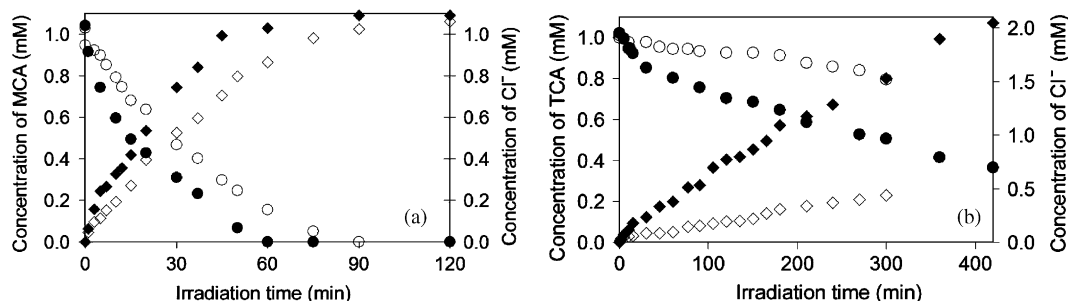


Fig. 7. Photodegradation of MCA (a) and TCA (b) using bare and silver-deposited P25 TiO_2 particles. Disappearance of CIAAs over TiO_2 (\circ) and over $\text{Ag}^0\text{-TiO}_2$ (\bullet) and formation of Cl^- over TiO_2 (\diamond) and over $\text{Ag}^0\text{-TiO}_2$ (\blacklozenge); $[\text{CIAA}]_0 = 1 \text{ mM}$, 1.6 at.% $\text{Ag}^0\text{-TiO}_2$, $C_{\text{TiO}_2} = 1 \text{ g dm}^{-3}$.

The investigations have been extended to reaction mixture containing all CIAAs in the same initial concentration (1 mM). Representative data are given by Fig. 6.

These clearly indicate the importance of the adsorption properties in the photocatalytic degradation of CIAAs. Namely, MCA molecules are readily adsorbed on the surface of TiO_2 and hence they suppress the adsorption of DCA and TCA. This effect leads to a significant decrease in the conversion of DCA. The attack of hydroxyl radical (reaction (7)) formed by primary electron transfer from water to the hole as well as the direct and/or O_2 -mediated electron transfer (reactions (5) and (6)), that are effective for molecules adsorbed at the surface, cannot occur with high efficiency when the DCA is far from the surface. The effect of competitive adsorption is demonstrated, by two experimental facts: (1) The deviation between the conversion of MCA in the suspension of the three CIAAs and that of in the reaction mixture containing MCA alone is very small at the initial stage of the photocatalysis and it significantly increases with irradiation time. (2) The conversion DCA starts with a considerable smaller rate in the mixture of CIAAs than in pure DCA suspension. In addition it slightly increases with the conversion of MCA and then, after 60 min irradiation the conversion of MCA and DCA occurs with nearly the same rate until ca. 150 min irradiation.

The photodegradation rate of TCA in the reaction mixture of the three acids has been found to be the same (within the experimental error) as observed under illumination of suspension containing TCA as single reactant. It is important to note that the plot of chloride concentration vs. irradiation time shows a breakpoint at the complete consumption of DCA in the reaction mixture of CIAAs (see FigS8). It is attributed to stopping of the efficient hydroxyl radical attack on the substrate and thus it confirms again the significant difference between the photodegradation mechanism of DCA and TCA, respectively.

3.4. Photodegradation of CIAAs over silver-deposited TiO_2

Deposition of silver clusters on the surface of TiO_2 has been found as an efficient method to improve the activity the semiconductor particles for photodegradation of various organic compounds [38,43–45]. However, the results of detailed studies indicated that it cannot be considered as a universal procedure to enhance the efficiency of photocatalyst [44,47]. The increase of the photocatalytic activity depends on the molecular structure of the substrate determining the mechanism of electron transfer reaction occurring at the surface of excited semiconductor particle. On the contrary, silver deposition can be applied as a tool for elucidating the mechanism of a given semiconductor-based heterogeneous photoreaction as it has been demonstrated recently [45]. Fig. 7 compares the decrease in the concentration of the reactants and formation of chloride ions under irradiation of MCA and TCA over bare and silver-deposited P25 TiO_2 ,

respectively. Using silver-deposited titania instead of bare semiconductor the initial photodegradation rate of MCA as well as that of DCA (see FigS9) increases slightly: by a factor of 1.4 for MCA and 1.5 for DCA. It should be noted that the same (1.4–1.5) enhancement has been measured for the yield of hydroxyl radical using COU in the presence of silver-deposited Degussa P25 TiO_2 [45]. This data supports our assumption, whereas the hydroxyl radical attack on MCA and DCA is the rate-determining step of the photodegradation of these acids. On the other hand, the initial rate of photodecomposition of TCA significantly increases (by a factor of ~ 4) when the irradiation is carried out over Ag-TiO_2 instead of bare TiO_2 .

Such an enhancement was observed for oxalic acid [38] reacting directly with the hole constituent of the photogenerated $\{\text{h}^+_{\text{VB}}; \text{e}^-_{\text{CB}}\}$ pair. Hence it is reasonable to conclude that one of these charge carriers is responsible for the photodegradation of TCA. Because chloride ion is detected as a primary product and this species is formed in stoichiometric ratio we strongly believe that it is the electron transfer from CB to TCA that, as primary step, initiates the degradation of TCA. Comparing the results obtained by photodegradation of TCA in aerobic and anaerobic conditions it should be emphasized that the initial decomposition rates of TCA over bare TiO_2 were found to be the same. So the efficiency of the direct electron transfer and the molecular oxygen mediated electron transfer to the TCA should be equivalent. It can be explained by a very fast electron transfer from $\text{O}_2^{\bullet-}_{\text{surf}}$ to TCA_{surf} .

4. Conclusions

Photocatalytic degradation of CIAAs over various bare (pure anatase, pure rutile and Degussa P25) and silver-deposited Degussa P25 TiO_2 particles was studied in aerobic and anaerobic conditions. The experiments were extended to investigate the adsorption characteristics of the substrates using TiO_2 photocatalysts of different nature. The progress of photocatalytic reaction was followed by measuring of the concentration of CIAAs, the total organic carbon content, the concentration of the chloride ion and the pH of the liquid phase of reaction mixtures. Moreover CO_2 evolution under photodegradation of DCA was also investigated.

By considering the opposite trends in the photodecomposition rate of CIAAs obtained for aerobic $v_{\text{MCA}} \approx v_{\text{DCA}} > v_{\text{TCA}}$ and for anaerobic experiments $v_{\text{TCA}} > v_{\text{DCA}} > v_{\text{MCA}}$, respectively, by exploiting the advantageous of using coumarin as luminescent probe for hydroxyl radical in competitive kinetic studies and by applying silver-deposited P25 TiO_2 for enhancing the separation of photo-generated charges at the surface of the semiconductor a significant progress in revealing the photodegradation mechanism of the investigated acids has been achieved. It has been found that the decomposition of MCA is dominantly initiated by hydroxyl radical attack. In contrast, it is the direct electron transfer from excited TiO_2

to the substrate that exclusively induces the degradation of TCA in anaerobic conditions. It has been suggested that in aerobic conditions the electron transfer to TCA is mediated by molecular oxygen at the surface of TiO₂ particle. The photodecomposition of DCA, similarly to that of MCA is dominantly initiated by hydroxyl radical attack in aerobic conditions.

This study demonstrates the effectiveness of combining the use of coumarin as selective scavenger of the free hydroxyl radicals and the enhanced charge separation achieved by deposition of silver clusters onto TiO₂ surface for mechanistic purposes in heterogeneous photocatalysis. It is also remarkable for applied research and for water technology development that the photomineralization rate of TCA, which is a hardly degradable compound, has been significantly increased by silver-deposited TiO₂.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apcatb.2008.12.012](https://doi.org/10.1016/j.apcatb.2008.12.012).

References

- [1] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.
- [2] A. Mills, S. Le Hunte, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 1.
- [3] D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993.
- [4] A. Fujishima, K. Hashimoto, T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, BKC. Publ., Tokyo, 1999.
- [5] A. Fujishima, T.N. Rao, D.A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.* 1 (2000) 1.
- [6] M. Kaneko, I. Okura (Eds.), *Photocatalysis (Science and Technology)*, Kodansha Tokyo, Springer-Verlag, Berlin, 2003.
- [7] D. Chatterjee, S. Dasgupta, *J. Photochem. Photobiol. C: Photochem. Rev.* 6 (2005) 186.
- [8] J. Wang, H. Gu, Y. Zhu, *Mod. Sci. Instrum.* 5 (2001) 60.
- [9] D.A. Ellis, M.L. Hanson, P.K. Sibley, T. Shahid, N.A. Fineberg, K.R. Solomon, D.C.G. Muir, S.A. Mabury, *Chemosphere* 42 (2001) 309.
- [10] Y. Li, Y. Xie, S. Peng, G. Lu, S. Li, *Chemosphere* 63 (2006) 1312.
- [11] E. Malliarou, C. Collins, N. Graham, M.J. Nieuwenhuijsen, *Water Res.* 39 (2005) 2722.
- [12] T. Reemtsma, M. Jekel, *Water Res.* 31 (1997) 1035.
- [13] D. Spangenberg, U. Möller, K. Kleinermaß, *Chemosphere* 33 (1996) 43.
- [14] D.F. Ollis, C.-Y. Hsiao, L. Budiman, C.-L. Lee, *J. Catal.* 88 (1984) 89.
- [15] A. Chemseddine, H.P. Boehm, *J. Mol. Catal.* 60 (1990) 295.
- [16] D.W. Bahnemann, M. Hilgendorff, R. Memming, *J. Phys. Chem. B* 101 (1997) 4265.
- [17] D.W. Bahnemann, S.N. Kholuisakaya, R. Dillert, A.I. Kulak, A.I. Kokorin, *Appl. Catal. B: Environ.* 36 (2002) 161.
- [18] L.L. Lifongo, D.J. Bowden, P. Brimblecombe, *Chemosphere* 55 (2004) 467.
- [19] K. Hirano, H. Nitta, K. Sawada, *Ultrason. Sonochem.* 12 (2005) 271.
- [20] B. Kraeutler, A.J. Bard, *J. Am. Chem. Soc.* 100 (1978) 5985.
- [21] C.S. Zalazar, R.L. Romero, C.A. Martín, A.E. Cassano, *Chem. Eng. Sci.* 60 (2005) 5240.
- [22] C.S. Zalazar, C.A. Martín, A.E. Cassano, *Chem. Eng. Sci.* 60 (2005) 4311.
- [23] N.R. Smith, P.A. Leighton, W.G. Leighton, *J. Am. Chem. Soc.* 61 (1939) 2299.
- [24] Y. Mao, C. Schoneich, K. Asmus, *J. Phys. Chem.* 95 (1991) 10080.
- [25] M.I. Litter, *Appl. Catal. B: Environ.* 23 (1999) 89.
- [26] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, *J. Photochem. Photobiol. A: Chem.* 148 (2002) 233.
- [27] D. Dvoranová, V. Brezová, M. Mazúr, M.A. Malati, *Appl. Catal. B: Environ.* 37 (2002) 91.
- [28] M. Bellardita, M. Addamo, A. Di Paola, L. Palmisano, *Chem. Phys.* 339 (2007) 94.
- [29] A. Sclafani, J.-M. Herrmann, *J. Photochem. Photobiol. A: Chem.* 113 (1998) 181.
- [30] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, *Chem. Eng. J.* 98 (2004) 127.
- [31] S.W. Lam, K. Chiang, T.M. Lim, R. Amal, G.K.-C. Low, *Appl. Catal. B: Environ.* 72 (2007) 363.
- [32] H. Tada, K. Teranishi, Y.I. Inubushi, S. Ito, *Chem. Commun.* 21 (1998) 2345.
- [33] H. Tada, K. Teranishi, Y.I. Inubushi, S. Ito, *Langmuir* 16 (2000) 3304.
- [34] L. Zhang, J.C. Yu, *Catal. Commun.* 6 (2005) 684.
- [35] A. Sclafani, M.N. Mozzanega, P. Pichat, *J. Photochem. Photobiol. A: Chem.* 59 (1991) 181.
- [36] J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, G. Lassaletta, A.R. González-Elipé, A. Fernández, *Appl. Catal. B: Environ.* 13 (1997) 219.
- [37] V. Vamathevan, H. Tse, R. Amal, G. Low, S. McEvoy, *Catal. Today* 68 (2001) 201.
- [38] E. Szabó-Bárdos, H. Czili, A. Horváth, *J. Photochem. Photobiol. A: Chem.* 154 (2003) 195.
- [39] S.X. Liu, Z.P. Qu, X. W. Han, C.L. Sun, *Catal. Today* 93–95 (2004) 877.
- [40] M. Moonsiri, P. Rangsunvigit, S. Chavadej, E. Gulari, *Chem. Eng. J.* 97 (2004) 241.
- [41] D. Shchukin, E. Ustinovich, D. Sviridov, P. Pichat, *Photochem. Photobiol. Sci.* 3 (2004) 142.
- [42] X. You, F. Chen, J. Zhang, M. Anpo, *Catal. Lett.* 102 (2005) 247.
- [43] H.M. Coleman, K. Chiang, R. Amal, *Chem. Eng. J.* 113 (2005) 65.
- [44] H. Tran, K. Chiang, J. Scott, R. Amal, *Photochem. Photobiol. Sci.* 4 (2005) 565.
- [45] E. Szabó-Bárdos, E. Pétervári, V. El-Zein, A. Horváth, *J. Photochem. Photobiol. A: Chem.* 184 (2006) 221.
- [46] A. Vohra, D.Y. Goswami, D.A. Deshpande, S.S. Block, *Appl. Catal. B: Environ.* 65 (2006) 57.
- [47] H. Tran, J. Scott, K. Chiang, R. Amal, *J. Photochem. Photobiol. A: Chem.* 183 (2006) 41.
- [48] C.G. Hatchard, C.A. Parker, *Proc. Roy. Soc. (Lond.) A* 235 (1956) 518.
- [49] G.V. Buxton, C.L. Greenstock, W.P. Helma, A.B. Ross, *Phys. Chem. Ref. Data* 17 (1988) 513.
- [50] D. Lawless, N. Serpone, D. Meisel, *J. Phys. Chem.* 95 (1991) 5166.
- [51] J. Giménez, M.A. Augado, S. Cervera-March, *J. Mol. Catal. A: Chem.* 105 (1996) 67.
- [52] K.-i. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, *Electrochem. Commun.* 2 (2000) 207.
- [53] K.-i. Ishibashi, A. Fujishima, T. Watanabe, K. Hashimoto, *J. Photochem. Photobiol. A: Chem.* 134 (2000) 139.
- [54] H. Czili, A. Horváth, *Appl. Catal. B: Environ.* 81 (2008) 295.
- [55] The rate coefficient of reactions $^{\bullet}\text{OH} + \text{ClCH}_2\text{COO}^-$ and $^{\bullet}\text{OH} + \text{Cl}_2\text{CHCOO}^-$ has been estimated by the results of these competitive kinetic measurements; $k_{\text{MCA}} = 8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{DCA}} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.